NAME: M.A. Boggs
ORGANIZATION: Lawrence Livermore National Laboratory
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: A Survey of Plutonium Sorption Behavior in Ternary Pu-DOM-Mineral Systems and Novel Spectroscopies to Probe Their Molecular Structure

ABSTRACT: The Subsurface Biogeochemical Research (SBR) Scientific Focus Area (SFA) at Lawrence Livermore National Laboratory is focused on identification and quantification of the biogeochemical processes that control the fate and transport of Pu. The second of five program elements is focused on quantifying the sorption/desorption behavior of ternary surface complexes at environmentally relevant Pu concentrations. Here, we present results of this program element as well as early results from our microbiological investigations.

We have studied the effect of Pu in the presence of montmorillonite with three organic ligands: humic acid (HA), fulvic acid (FA), and deferrioxamine B (DFOB). A decrease in Pu sorption relative to a ligand free system was observed over a wide pH range in systems containing HA and FA. The results suggest a relatively straightforward competition reaction between montmorillonite and HA for Pu complexation and a weaker influence of FA. Conversely, DFOB led to an increase in Pu(IV) sorption. Montmorillonite was able to sorb up to1 mM DFOB/g mineral. Both TEM and XRD indicated an increase in montmorillonite interlayer spacing from 10 to 18 Å with the addition of DFOB.

The unique behavior of the Pu(IV)-DFOB complex led to structural characterization studies by NMR which combined with UV-Vis identified two distinct complexes. Conversion between the two complexes was rapid as the pH shifted below or above ~ 4. ^{1}H spectra of the complexes show a large amount of peak broadening and chemical shifts which can be associated with changes in conformation and the presence of a paramagnetic metal center. Peak assignments were made through the 2D techniques of Correlation Spectroscopy (COSY) and Heteronuclear Single Quantum Correlation (HSQC). Variable temperature ^{1}H spectra were acquired and we were able to observe pseudo contact shifts (PCS) and determine the distance of the shifted protons from the metal center. Diffusion Ordered Spectroscopy (DOSY) was used to determine the rates of diffusion and size of the two Pu(IV)-DFOB complexes. These results indicate that the complex at pH 7.0 is on the order of twice the size of the lower pH complex. The high pH complex was previously identified[1] as Pu(IV)DFOB$(OH)_2$, while our results suggest that it is more likely a dimeric DFOBPu(IV)di-μ-OH-DFOBPu(IV) species.

Sorption of Pu(IV) to a number of other mineral surfaces in the presence of natural organic matter (NOM) was examined using a combination of batch sorption and Fourier Transform Infrared Spectroscopy (FTIR). Tritium labeled fulvic and humic acid and ^{14}C labeled citric acid were used to lower the NOM detection limits and observe sorption of NOM and ^{238}Pu simultaneously. In general, the results indicate the possibility of ternary surface complex formation at low pH which will enhance sorption relative to a ligand free system and solubilization of Pu at high pH due to aqueous complexation with

NOM. The formation of ternary complexes will require that NOM serve as a sorbed, bridging ligand. The existence of specifically sorbed NOM complexes has been examined and confirmed using FTIR.

Prepared by LLNL under Contract DE-AC52-07NA27344.

[1] Boukhalfa, H.; Reilly, S.; Neu, M., *Inorganic Chemistry* **2007,** *46*, 1018-1026.